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(54) Title: CLEANSING PRODUCTS (57) Abstract The present invention relates to a substantially dry, disposable, personal cleansing product useful for both cleansing and conditioning the skin or hair. These products are used by the consumer by wetting the dry product with water. The product comprises a water insoluble substrate, a lathering surfactant, and an oil soluble conditioning agent. The invention also encompasses methods for cleansing and conditioning the skin or hair using these products and to methods for manufacturing these products.		

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CLEANSING PRODUCTS

TECHNICAL FIELD

The present invention relates to a substantially dry, disposable, personal cleansing product useful for both cleansing and conditioning the skin or hair. These products are used by the consumer by wetting the dry product with water. The product comprises a water insoluble substrate, a lathering surfactant, and an oil soluble conditioning agent.

Use of the substrate enhances lathering at low surfactant levels, increases cleansing and exfoliation, and optimizes delivery and deposition of conditioning ingredients. As a result, this invention provides effective cleansing using low, and hence less irritating, levels of surfactant while providing superior conditioning benefits.

The invention also encompasses products comprising various active ingredients for delivery to the skin or hair.

The invention also encompasses a method for cleansing and moisturizing the skin and hair using the products of the present invention and also to methods for manufacturing these products.

BACKGROUND OF THE INVENTION

Personal cleansing products have traditionally been marketed in a variety of forms such as bar soaps, creams, lotions, and gels. These cleansing formulations have attempted to satisfy a number of criteria to be acceptable to consumers. These criteria include cleansing effectiveness, skin feel, mildness to skin, hair, and ocular mucosae, and lather volume. Ideal personal cleansers should gently cleanse the skin or hair, cause little or no irritation, and not leave the skin or hair overly dry after frequent use.

However, these traditional forms of personal cleansing products have the inherent problem of balancing cleansing efficacy against delivering a conditioning benefit. One solution to this problem is to use separate cleansing and conditioning products. However, this is not always convenient or practical and many consumers would prefer to use a single product which can both cleanse and condition the skin or hair. In a typical cleansing composition the conditioning ingredients are difficult to formulate because many conditioners are incompatible with the surfactants, resulting in an undesirable non-homogenous mixture. To obtain a homogeneous mixture with conditioning ingredients, and to prevent the loss of conditioning ingredients before deposition, additional ingredients, e.g. emulsifiers, thickeners, and gellants are often

added to suspend the conditioning ingredients within the surfactant mixture. This results in an aesthetically pleasing homogenous mixture, but often results in poor deposition of conditioning ingredients, because the conditioners are emulsified and not efficiently released during cleansing. Also, many conditioning agents have the disadvantage of suppressing lather generation. Lather suppression is a problem because many consumers seek cleansing products that provide a rich, creamy, and generous lather.

Therefore, it is seen that conventional cleansing products which attempt to combine surfactants and conditioning ingredients suffer from disadvantages inherently resulting from the incompatibilities of surfactants and conditioners. A need clearly exists to develop cleansing systems which provide effective cleansing and yet provide sufficient conditioning in a single product.

It is also highly desirable to deliver cleansing and conditioning benefits from a disposable, single use product. Disposable products are convenient because they obviate the need to carry cumbersome bottles, bars, jars, tubes, and other forms of both cleansing and conditioning products. Disposable products are also a more sanitary alternative to the use of a sponge, washcloth, or other cleansing implement intended for multiple reuse, because such implements develop bacterial growth, unpleasant odors, and other undesirable characteristics related to repeated use.

It has been surprisingly found in the present invention that products can be developed to provide effective cleansing and conditioning in a convenient, inexpensive, and sanitary disposable personal cleansing product. The present invention provides the convenience of not needing to use both a separate cleansing and conditioning product. The present invention is highly convenient to use because it is in the form of a substantially dry product that is wetted before use.

The present invention relates to a dry, disposable, personal cleansing product useful for both cleansing and conditioning the skin or hair. These products are used by the consumer by wetting the dry product with water. The product consists of a water insoluble substrate, a surfactant, and a conditioner. Without being limited by theory, it is believed that the substrate enhances lathering at low surfactant levels, increases cleansing and exfoliation, and optimizes delivery and deposition of the conditioning ingredients. As a result, this invention provides effective cleansing using low, and hence less irritating, levels of surfactant while providing superior conditioning benefits. It has also been found that these products are useful for delivering a wide range of active ingredients to the skin or hair during the cleansing process.

It is therefore, an object of the present invention to provide substantially dry products for both cleansing and conditioning the skin or hair wherein the products are used in combination with water.

It is another object of the present invention to provide products comprising a water insoluble substrate, a surfactant, and a conditioner component.

It is another object of the present invention to provide products which are disposable and intended for single use.

It is another object of the present invention to provide products which are mild to the skin or hair.

It is another object of the present invention to provide products useful for delivering active ingredients to the skin or hair during the cleansing and conditioning process.

It is another object of the present invention to provide methods of cleansing and conditioning the skin or hair.

It is another object of the present invention to provide methods of manufacturing the products of the present invention.

These and other objects of this invention will become apparent in light of the following disclosure.

SUMMARY OF THE INVENTION

The present invention relates to a disposable, single use personal care cleansing and conditioning product comprising:

- (A) a water insoluble substrate,
- (B) a lathering surfactant, and
- (C) an oil soluble conditioning agent,

wherein said cleansing product deposits greater than about $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and wherein said product is substantially dry.

In further embodiments, the present invention relates to disposable, single use personal care cleansing and conditioning product comprising:

- (A) a water insoluble substrate, and
- (B) a cleansing and conditioning composition comprising:
 - (i) a lathering surfactant, and
 - (ii) an oil soluble conditioning agent,

wherein said lathering surfactant and said oil soluble conditioning agent are separately or simultaneously added onto or impregnated into said water insoluble substrate, and wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than about 20:1, wherein said cleansing product deposits greater than

about $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and wherein said product is substantially dry.

In further embodiments, the present invention relates to a method of manufacturing a disposable, single use personal care cleansing and conditioning product comprising the step of separately or simultaneously adding onto or impregnating into a water insoluble substrate

- (A) a lathering surfactant, and
- (B) an oil soluble conditioning agent,

wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than about 20:1, wherein said cleansing product deposits greater than about $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and wherein said resulting product is substantially dry.

In further embodiments, the present invention relates to methods for cleansing and conditioning the skin or hair with the personal cleansing products described herein.

In even further embodiments, the present invention relates to methods of depositing conditioning agents to the skin or hair.

All percentages and ratios used herein, unless otherwise indicated, are by weight and all measurements made are at 25°C , unless otherwise designated. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described therein.

DETAILED DESCRIPTION OF THE INVENTION

The personal cleansing products of the present invention are highly efficacious for cleansing the skin or hair, yet, provide effective deposition of conditioning agents. The products can also contain other active ingredients to be deposited onto the skin or hair.

Without being limited by theory it is believed that the substrate significantly contributes to generation of lather and deposition of conditioning agents and any other active ingredients. It is believed that this increase in lathering is the result of the surface action of the substrate. As a result, milder and significantly lower amounts of surfactants may be employed. The decreased amount of required surfactant is believed to relate to the decrease in the drying effect of the skin or hair by the surfactants. Furthermore, the decreased amount of surfactant dramatically lowers the inhibitory action (e.g., via emulsification or direct removal by the surfactants) of surfactants to deposition of conditioning agents.

Without being limited by theory, the substrate also enhances deposition of conditioning agents and active ingredients. Since the invention is in dry form, the

invention does not require emulsifiers, which inhibit deposition of conditioning agents and active ingredients. Furthermore, because the skin conditioners and active ingredients are dried onto or impregnated into the substrate, they are transferred directly to the skin or hair by surface contact of the wetted product to the skin.

Finally, the substrate also enhances cleansing. The substrate can have differing textures on each side, e.g. a rough side and a smooth side. The substrate acts as an efficient lathering and exfoliating implement. By physically coming into contact with the skin or hair, the substrate significantly aids in cleansing and removal of dirt, makeup, dead skin, and other debris.

By a "lathering surfactant" is meant a surfactant, which when combined with water and mechanically agitated generates a foam or lather. Preferably, these surfactants should be mild, which means that these surfactants provide sufficient cleansing or deterative benefits but do not overly dry the skin or hair, and yet meet the lathering criteria described above.

The terms "disposable" or "single use", are used herein in their ordinary sense to mean a product that is disposed or discarded after one usage event.

The term "water-activated," as used herein, means that the present invention is presented to the consumer in dry form to be used after wetting with water. It is found that these products produce a lather or are "activated" upon contact with water and further agitation.

The term "substantially dry" as used herein means that the product is substantially free of water and generally feels dry to the touch. The products of the present invention comprise less than about 10% by weight of water, preferably less than about 5% by weight of water, and more preferably less than about 1% by weight of water, the foregoing measured in a dry environment, e.g., low humidity. One of ordinary skill in the art would recognize that the water content of a product such as in the present invention can vary with the relative humidity of the environment.

The term "mild" as used herein in reference to the lathering surfactants and products of the present invention means that the products of the present invention demonstrate skin mildness comparable to a mild alkyl glyceryl ether sulfonate (AGS) surfactant based synthetic bar, i.e. synbar. Methods for measuring mildness, or inversely the irritancy, of surfactant containing products, are based on a skin barrier destruction test. In this test, the milder the surfactant, the lesser the skin barrier is destroyed. Skin barrier destruction is measured by the relative amount of radio-labeled (tritium labeled) water ($3\text{H-H}_2\text{O}$) which passes from the test solution through the skin epidermis into the physiological buffer contained in the diffusate chamber. This test is described by T.J. Franz in the J. Invest. Dermatol., 1975, 64, pp. 190-195;

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and in U.S. Patent No. 4,673,525, to Small et al., issued June 16, 1987, which are both incorporated by reference herein in their entirety. Other testing methodologies for determining surfactant mildness well known to one skilled in the art can also be used.

The personal care products of the present invention comprise the following essential components. The composition which is either impregnated into or applied onto the substrate consists essentially of one or more surfactants and one or more conditioning agents. Additional active ingredients can also be included within the composition. An alternative, preferred method is to apply each ingredient separately to the substrate.

In embodiments where only an oil soluble conditioning agent is required, these cleansing and conditioning products are preferably substantially free of C12-15 alcohols benzoates, i.e. free of benzoic acid esters of alcohols having primarily from about 12 to about 15 carbon atoms. See, International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, p 87, which is incorporated by reference herein in its entirety. Also, "substantially free of C12-15 alcohols benzoates" means less than about 1%, preferably less than about 0.5%, and more preferably less than about 0.25%, by weight of the cleansing and conditioning composition, which comprises the lathering surfactant and the oil soluble conditioning agent.

WATER INSOLUBLE SUBSTRATE

The products of the present invention comprise a water insoluble substrate. By "water insoluble" is meant that the substrate does not dissolve in or readily break apart upon immersion in water. The water insoluble substrate is the implement or vehicle for delivering the lathering surfactant and the conditioning component of the present invention to the skin or hair to be cleansed and conditioned. Without being limited by theory, it is believed that the substrate, by providing mechanical agitation provides a lather generating effect and also aids in the deposition of the conditioning component.

A wide variety of materials can be used as the substrate. The following nonlimiting characteristics are desirable: (i) sufficient wet strength for use, (ii) sufficient abrasivity, (iii) sufficient loft and porosity, (iv) sufficient thickness, and (v) appropriate size.

Nonlimiting examples of suitable insoluble substrates which meet the above criteria include nonwoven substrates, woven substrates, hydroentangled substrates, air entangled substrates, natural sponges, synthetic sponges, polymeric netted meshes, and the like. Preferred embodiments employ nonwoven substrates since they are economical and readily available in a variety of materials. By nonwoven is meant

that the layer is comprised of fibers which are not woven into a fabric but rather are formed into a sheet, mat, or pad layer. The fibers can either be random (i.e., randomly aligned) or they can be carded (i.e. combed to be oriented in primarily one direction). Furthermore, the nonwoven substrate can be composed of a combination of layers of random and carded fibers.

Nonwoven substrates may be comprised of a variety of materials both natural and synthetic. By natural is meant that the materials are derived from plants, animals, insects or byproducts of plants, animals, and insects. By synthetic is meant that the materials are obtained primarily from various man-made materials or from natural materials which have been further altered. The conventional base starting material is usually a fibrous web comprising any of the common synthetic or natural textile-length fibers, or mixtures thereof.

Nonlimiting examples of natural materials useful in the present invention are silk fibers, keratin fibers and cellulosic fibers. Nonlimiting examples of keratin fibers include those selected from the group consisting of wool fibers, camel hair fibers, and the like. Nonlimiting examples of cellulosic fibers include those selected from the group consisting of wood pulp fibers, cotton fibers, hemp fibers, jute fibers, flax fibers, and mixtures thereof.

Nonlimiting examples of synthetic materials useful in the present invention include those selected from the group consisting of acetate fibers, acrylic fibers, cellulose ester fibers, modacrylic fibers, polyamide fibers, polyester fibers, polyolefin fibers, polyvinyl alcohol fibers, rayon fibers, polyurethane foam, and mixtures thereof. Examples of some of these synthetic materials include acrylics such as acrilan, creslan, and the acrylonitrile-based fiber, orlon; cellulose ester fibers such as cellulose acetate, arnel, and acele; polyamides such as nylons (e.g., nylon 6, nylon 66, nylon 610, and the like); polyesters such as fortrel, kodel, and the polyethylene terephthalate fiber, dacron; polyolefins such as polypropylene, polyethylene; polyvinyl acetate fibers; polyurethane foams and mixtures thereof. These and other suitable fibers and the nonwoven materials prepared therefrom are generally described in Riedel, "Nonwoven Bonding Methods and Materials," Nonwoven World (1987); The Encyclopedia Americana, vol. 11, pp. 147-153, and vol. 26, pp. 566-581 (1984); U.S. Patent No. 4,891,227, to Thaman et al., issued January 2, 1990; and U.S. Patent No. 4,891,228 which are all incorporated by reference herein in their entirety.

Nonwoven substrates made from natural materials consist of webs or sheets most commonly formed on a fine wire screen from a liquid suspension of the fibers. See C.A. Hampel et al., The Encyclopedia of Chemistry, third edition, 1973, pp. 793-795 (1973); The Encyclopedia Americana, vol. 21, pp. 376-383 (1984); and G.A.

Smook, Handbook of Pulp and Paper Technologies, Technical Association for the Pulp and Paper Industry (1986); which are incorporated by reference herein in their entirety.

Substrates made from natural materials useful in the present invention can be obtained from a wide variety of commercial sources. Nonlimiting examples of suitable commercially available paper layers useful herein include Airtex^R, an embossed airlaid cellulosic layer having a base weight of about 71 gsy, available from James River, Green Bay, WI; and Walkisoft^R, an embossed airlaid cellulosic having a base weight of about 75 gsy, available from Walkisoft U.S.A., Mount Holly, NC.

Methods of making nonwoven substrates are well known in the art. Generally, these nonwoven substrates can be made by air-laying, water-laying, meltblowing, coforming, spunbonding, or carding processes in which the fibers or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fiber-laden air or water is passed. The resulting layer, regardless of its method of production or composition, is then subjected to at least one of several types of bonding operations to anchor the individual fibers together to form a self-sustaining web. In the present invention the nonwoven layer can be prepared by a variety of processes including hydroentanglement, thermally bonding or thermo-bonding, and combinations of these processes. Moreover, the substrates of the present invention can consist of a single layer or multiple layers. In addition, a multilayered substrate can include films and other nonfibrous materials.

Nonwoven substrates made from synthetic materials useful in the present invention can also be obtained from a wide variety of commercial sources. Nonlimiting examples of suitable nonwoven layer materials useful herein include HEF 40-047, an apertured hydroentangled material containing about 50% rayon and 50% polyester, and having a basis weight of about 43 grams per square yard (gsy), available from Veratec, Inc., Walpole, MA; HEF 140-102, an apertured hydroentangled material containing about 50% rayon and 50% polyester, and having a basis weight of about 56 gsy, available from Veratec, Inc., Walpole, MA; Novonet^R 149-616, a thermo-bonded grid patterned material containing about 100% polypropylene, and having a basis weight of about 50 gsy, available from Veratec, Inc., Walpole, MA; Novonet^R 149-801, a thermo-bonded grid patterned material containing about 69% rayon, about 25% polypropylene, and about 6% cotton, and having a basis weight of about 75 gsy, available from Veratec, Inc. Walpole, MA; Novonet^R 149-191, a thermo-bonded grid patterned material containing about 69% rayon, about 25% polypropylene, and about 6% cotton, and having a basis weight of

about 100 gsy, available from Veratec, Inc. Walpole, MA; HEF Nubtex^R 149-801, a nubbed, apertured hydroentangled material, containing about 100% polyester, and having a basis weight of about 70 gsy, available from Veratec, Inc. Walpole, MA; Keybak^R 951V, a dry formed apertured material, containing about 75% rayon, about 25% acrylic fibers, and having a basis weight of about 43 gsy, available from Chicopee, New Brunswick, NJ; Keybak^R 1368, an apertured material, containing about 75% rayon, about 25% polyester, and having a basis weight of about 39 gsy, available from Chicopee, New Brunswick, NJ; Duralace^R 1236, an apertured, hydroentangled material, containing about 100% rayon, and having a basis weight from about 40 gsy to about 115 gsy, available from Chicopee, New Brunswick, NJ; Duralace^R 5904, an apertured, hydroentangled material, containing about 100% polyester, and having a basis weight from about 40 gsy to about 115 gsy, available from Chicopee, New Brunswick, NJ; Sontaro 8868, a hydroentangled material, containing about 50% cellulose and about 50% polyester, and having a basis weight of about 60 gsy, available from Dupont Chemical Corp.

Alternatively, the water insoluble substrate can be a polymeric mesh sponge as described in European Patent No. EP 702550 A1 published March 27, 1996, incorporated by reference herein in its entirety. The polymeric sponge comprises a plurality of plies of an extruded tubular netting mesh prepared from a strong flexible polymer, such as addition polymers of olefin monomers and polyamides of polycarboxylic acids. Although these polymeric sponges are designed to be used in conjunction with a liquid cleanser, these types of sponges can be used as the water insoluble substrate in the present invention.

The substrate can be made into a wide variety of shapes and forms including flat pads, thick pads, thin sheets, ball-shaped implements, irregularly shaped implements, and having sizes ranging from a surface area of about a square inch to about hundreds of square inches. The exact size will depend upon the desired use and product characteristics. Especially convenient are square, circular, rectangular, or oval pads having a surface area of from about 1 in² to about 144 in², preferably from about 10 in² to about 120 in², and more preferably from about 30 in² to about 80 in², and a thickness of from about 1 mil to about 500 mil, preferably from about 5 mil to about 250 mil, and more preferably from about 10 mil to about 100 mil.

The water insoluble substrates of the present invention can comprise two or more layers, each having different textures and abrasiveness. The differing textures can result from the use of different combinations of materials or from the use of different manufacturing processes or a combination thereof. A dual textured substrate can be made to provide the advantage of having a more abrasive side for

exfoliation and a softer, absorbent side for gentle cleansing. In addition, separate layers of the substrate can be manufactured to have different colors, thereby helping the user to further distinguish the surfaces.

LATHERING SURFACTANT

The products of the present invention comprise from about 0.5% to about 12.5%, preferably from about 0.75% to about 11%, and more preferably from about 1% to about 10%, based on the weight of the water insoluble substrate, of a lathering surfactant.

By a lathering surfactant is meant a surfactant, which when combined with water and mechanically agitated generates a foam or lather. Preferably, these surfactants or combinations of surfactants should be mild, which means that these surfactants provide sufficient cleansing or deterative benefits but do not overly dry the skin or hair, and yet meet the lathering criteria described above.

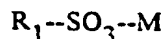
A wide variety of lathering surfactants are useful herein and include those selected from the group consisting of anionic lathering surfactants, nonionic lather surfactants, amphoteric lathering surfactants, and mixtures thereof. Cationic surfactants can also be used as optional components, provided they do not negatively impact the overall lathering characteristics of the required, lathering surfactants.

Anionic Lathering Surfactants

Nonlimiting examples of anionic lathering surfactants useful in the compositions of the present invention are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; McCutcheon's, Functional Materials, North American Edition (1992); and U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975 all of which are incorporated by reference herein in their entirety.

A wide variety of anionic lathering surfactants are useful herein. Nonlimiting examples of anionic lathering surfactants include those selected from the group consisting of sarcosinates, sulfates, isethionates, taurates, phosphates, and mixtures thereof. Amongst the isethionates, the alkoyl isethionates are preferred, and amongst the sulfates, the alkyl and alkyl ether sulfates are preferred. The alkoyl isethionates typically have the formula $\text{RCO-OCH}_2\text{CH}_2\text{SO}_3\text{M}$ wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Nonlimiting examples of these isethionates include those alkoyl isethionates selected from the group consisting of ammonium cocoyl isethionate, sodium cocoyl isethionate, sodium lauroyl isethionate, and mixtures thereof.

The alkyl and alkyl ether sulfates typically have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, x is from about 1 to about 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 16, carbon atoms; and M is a cation. Still other anionic synthetic surfactants include the class designated as succinamates, olefin sulfonates having about 12 to about 24 carbon atoms, and b-alkyloxy alkane sulfonates. Examples of these materials are sodium lauryl sulfate and ammonium lauryl sulfate.

Other anionic materials include the sarcosinates, nonlimiting examples of which include sodium lauroyl sarcosinate, sodium cocoyl sarcosinate, and ammonium lauroyl sarcosinate.

Other anionic materials useful herein are soaps (i.e. alkali metal salts, e.g., sodium or potassium salts) of fatty acids, typically having from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. The fatty acids used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, soybean oil, castor oil, tallow, lard, etc.) The fatty acids can also be synthetically prepared. Soaps are described in more detail in U.S. Patent No. 4,557,853, cited above.

Other anionic materials include phosphates such as monoalkyl, dialkyl, and trialkylphosphate salts.

Other anionic materials include alkanoyl sarcosinates corresponding to the formula $\text{RCON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CO}_2\text{M}$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and trialkanolamine (e.g., triethanolamine), a preferred example of which is sodium lauroyl sarcosinate.

Also useful are taurates which are based on taurine, which is also known as 2-aminoethanesulfonic acid. Examples of taurates include N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072 which is incorporated herein by reference in its entirety.

Nonlimiting examples of preferred anionic lathering surfactants useful herein include those selected from the group consisting of sodium lauryl sulfate, ammonium

lauryl sulfate, ammonium laureth sulfate, sodium laureth sulfate, sodium trideceth sulfate, ammonium cetyl sulfate, sodium cetyl sulfate, ammonium cocoyl isethionate, sodium lauroyl isethionate, sodium lauroyl sarcosinate, and mixtures thereof.

Especially preferred for use herein is ammonium lauryl sulfate and ammonium laureth sulfate.

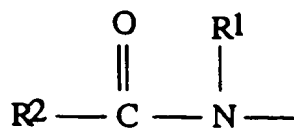
Nonionic Lathering Surfactants

Nonlimiting examples of nonionic lathering surfactants for use in the compositions of the present invention are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; and McCutcheon's, Functional Materials, North American Edition (1992); both of which are incorporated by reference herein in their entirety.

Nonionic lathering surfactants useful herein include those selected from the group consisting of alkyl glucosides, alkyl polyglucosides, polyhydroxy fatty acid amides, alkoxyated fatty acid esters, sucrose esters, amine oxides, and mixtures thereof.

Alkyl glucosides and alkyl polyglucosides are useful herein, and can be broadly defined as condensation products of long chain alcohols, e.g. C8-30 alcohols, with sugars or starches or sugar or starch polymers, i.e., glycosides or polyglycosides. These compounds can be represented by the formula $(S)_n-O-R$ wherein S is a sugar moiety such as glucose, fructose, mannose, and galactose; n is an integer of from about 1 to about 1000, and R is a C8-30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, and the like. Preferred examples of these surfactants include those wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from about 1 to about 9. Commercially available examples of these surfactants include decyl polyglucoside (available as APG 325 CS from Henkel) and lauryl polyglucoside (available as APG 600CS and 625 CS from Henkel). Also useful are sucrose ester surfactants such as sucrose cocoate and sucrose laurate.

Other useful nonionic surfactants include polyhydroxy fatty acid amide surfactants, more specific examples of which include glucosamides, corresponding to the structural formula:



wherein: R^1 is H, C_1 - C_4 alkyl, 2-hydroxyethyl, 2-hydroxy-propyl, preferably C_1 - C_4 alkyl, more preferably methyl or ethyl, most preferably methyl; R^2 is C_5 - C_{31} alkyl or alkenyl, preferably C_7 - C_{19} alkyl or alkenyl, more preferably C_9 - C_{17} alkyl or alkenyl, most preferably C_{11} - C_{15} alkyl or alkenyl; and Z is a polhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with a least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably is a sugar moiety selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose, and mixtures thereof. An especially preferred surfactant corresponding to the above structure is coconut alkyl N-methyl glucoside amide (i.e., wherein the R^2CO - moiety is derived from coconut oil fatty acids). Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd.; U.S. Patent No. 2,965,576, to E.R. Wilson, issued December 20, 1960; U.S. Patent No. 2,703,798, to A.M. Schwartz, issued March 8, 1955; and U.S. Patent No. 1,985,424, to Piggott, issued December 25, 1934; which are incorporated herein by reference in their entirety.

Other examples of nonionic surfactants include amine oxides. Amine oxides correspond to the general formula $R_1R_2R_3NO$, wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

Nonlimiting examples of preferred nonionic surfactants for use herein are those selected from the group consisting of C8-C14 glucose amides, C8-C14 alkyl polyglucosides, sucrose cocoate, sucrose laurate, lauramine oxide, cocoamine oxide, and mixtures thereof.

Amphoteric Lathering Surfactants

The term "amphoteric lathering surfactant," as used herein, is also intended to encompass zwitterionic surfactants, which are well known to formulators skilled in the art as a subset of amphoteric surfactants.

A wide variety of amphoteric lathering surfactants can be used in the compositions of the present invention. Particularly useful are those which are broadly described as derivatives of aliphatic secondary and tertiary amines, preferably wherein the nitrogen is in a cationic state, in which the aliphatic radicals can be straight or branched chain and wherein one of the radicals contains an ionizable water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

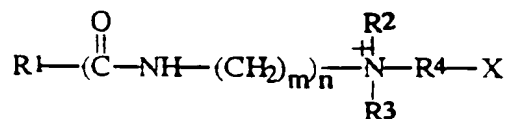
Nonlimiting examples of amphoteric surfactants useful in the compositions of the present invention are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; and McCutcheon's, Functional Materials, North American Edition (1992); both of which are incorporated by reference herein in their entirety.

Nonlimiting examples of amphoteric or zwitterionic surfactants are those selected from the group consisting of betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanoates, aminoalkanoates, and mixtures thereof.

Examples of betaines include the higher alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, cetyl dimethyl betaine (available as Lonzaine 16SP from Lonza Corp.), lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine, amidobetaines and amidosulfobetaines (wherein the $RCONH(CH_2)_3$ radical is attached to the nitrogen atom of the betaine), oleyl betaine (available as amphoteric Velvetex OLB-50 from Henkel), and cocamidopropyl betaine (available as Velvetex BK-35 and BA-35 from Henkel).

Examples of sultaines and hydroxysultaines include materials such as cocamidopropyl hydroxysultaine (available as Mirataine CBS from Rhone-Poulenc).

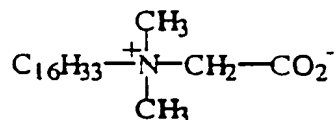
Preferred for use herein are amphoteric surfactants having the following structure:



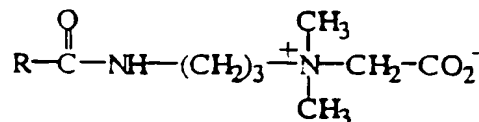
wherein R^1 is unsubstituted, saturated or unsaturated, straight or branched chain alkyl having from about 9 to about 22 carbon atoms. Preferred R^1 has from about 11 to about 18 carbon atoms; more preferably from about 12 to about 18 carbon atoms; more preferably still from about 14 to about 18 carbon atoms; m is an integer from 1 to about 3, more preferably from about 2 to about 3, and more preferably about 3; n is either 0 or 1, preferably 1; R^2 and R^3 are independently selected from the group consisting of alkyl having from 1 to about 3 carbon atoms, unsubstituted or mono-substituted with hydroxy, preferred R^2 and R^3 are CH_3 ; X is selected from the group consisting of CO_2 , SO_3 and SO_4 ; R^4 is selected from the group consisting of saturated or unsaturated, straight or branched chain alkyl, unsubstituted or monosubstituted with hydroxy, having from 1 to about 5 carbon atoms. When X is CO_2 , R^4 preferably has 1 or 3 carbon atoms, more preferably 1 carbon atom. When X is SO_3 or SO_4 , R^4 preferably has from about 2 to about 4 carbon atoms, more preferably 3 carbon atoms.

Examples of amphoteric surfactants of the present invention include the following compounds:

Cetyl dimethyl betaine (this material also has the CTFA designation cetyl betaine)



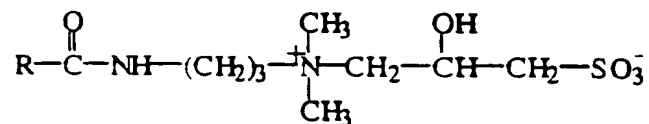
Cocamidopropylbetaine



wherein R has from about 9 to about 13 carbon atoms

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Cocamidopropyl hydroxy sultaine



wherein R has from about 9 to about 13 carbon atoms,

Examples of other useful amphoteric surfactants are alkyliminoacetates, and iminodialkanoates and aminoalkanoates of the formulas $\text{RN}(\text{CH}_2)_m\text{CO}_2\text{M}]_2$ and $\text{RNH}(\text{CH}_2)_m\text{CO}_2\text{M}$ wherein m is from 1 to 4, R is a C₈-C₂₂ alkyl or alkenyl, and M is H, alkali metal, alkaline earth metal ammonium, or alkanolammonium. Also included are imidazolinium and ammonium derivatives. Specific examples of suitable amphoteric surfactants include sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091 which is incorporated herein by reference in its entirety; and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378, which is incorporated herein by reference in its entirety. Other examples of useful amphoterics include amphoteric phosphates, such as coamidopropyl PG-dimonium chloride phosphate (commercially available as Monaquat PTC, from Mona Corp.). Also useful are amphotoacetates such as disodium lauroamphodiacetate, sodium lauroamphoacetate, and mixtures thereof.

Preferred lathering surfactants for use herein are the following, wherein the anionic lathering surfactant is selected from the group consisting of ammonium lauroyl sarcosinate, sodium trideceth sulfate, sodium lauroyl sarcosinate, ammonium laureth sulfate, sodium laureth sulfate, ammonium lauryl sulfate, sodium lauryl sulfate, ammonium cocoyl isethionate, sodium cocoyl isethionate, sodium lauroyl isethionate, sodium cetyl sulfate, and mixtures thereof; wherein the nonionic lathering surfactant is selected from the group consisting of lauramine oxide, cocoamine oxide, decyl polyglucose, lauryl polyglucose, sucrose cocoate, C12-14 glucosamides, sucrose laurate, and mixtures thereof; and wherein the amphoteric lathering surfactant is selected from the group consisting of disodium lauroamphodiacetate, sodium lauroamphoacetate, cetyl dimethyl betaine, cocoamidopropyl betaine, cocoamidopropyl hydroxy sultaine, and mixtures thereof.

CONDITIONING COMPONENT

The products of the present invention comprise a oil soluble conditioning agent which is useful for providing a conditioning benefit to the skin or hair during the use of the product. The oil soluble conditioning agent comprises from about 1%

to about 99%, preferably from about 2% to about 50%, and more preferably from about 3% to about 25% by weight of said water insoluble substrate.

The oil soluble conditioning agent is selected from one or more oil soluble conditioning agents such that the weighted arithmetic mean solubility parameter of the oil soluble conditioning agent is less than or equal to 10.5. It is recognized, based on this mathematical definition of solubility parameters, that it is possible, for example, to achieve the required weighted arithmetic mean solubility parameter, i.e. less than or equal to 10.5, for an oil soluble conditioning agent comprising two or more compounds if one of the compounds has an individual solubility parameter greater than 10.5.

Solubility parameters are well known to the formulation chemist of ordinary skill in the art and are routinely used as a guide for determining compatibility's and solubilities of materials in the formulation process.

The solubility parameter of a chemical compound, δ , is defined as the square root of the cohesive energy density for that compound. Typically, a solubility parameter for a compound is calculated from tabulated values of the additive group contributions for the heat of vaporization and molar volume of the components of that compound, using the following equation:

$$\delta = \left[\frac{\sum_i E_i}{\sum_i m_i} \right]^{1/2}$$

wherein $\sum_i E_i$ = the sum of the heat of vaporization additive group contributions, and

$\sum_i m_i$ = the sum of the molar volume additive group contributions

Standard tabulations of heat of vaporization and molar volume additive group contributions for a wide variety of atoms and groups of atoms are collected in Barton, A.F.M. Handbook of Solubility Parameters, CRC Press, Chapter 6, Table 3, pp. 64-66 (1985), which is incorporated by reference herein in its entirety. The above solubility parameter equation is described in Fedors, R.F., "A Method for Estimating Both the Solubility Parameters and Molar Volumes of Liquids", Polymer Engineering and Science, vol. 14, no. 2, pp. 147-154 (February 1974), which is incorporated by reference herein in its entirety.

Solubility parameters obey the law of mixtures such that the solubility parameter for a mixture of materials is given by the weighted arithmetic mean (i.e. the weighted average) of the solubility parameters for each component of that mixture. See, Handbook of Chemistry and Physics, 57th edition, CRC Press, p. C-726 (1976-1977), which is incorporated by reference herein in its entirety.

Formulation chemists typically report and use solubility parameters in units of $(\text{cal}/\text{cm}^3)^{1/2}$. The tabulated values of additive group contributions for heat of vaporization in the Handbook of Solubility Parameters are reported in units of kJ/mol. However, these tabulated heat of vaporization values are readily converted to cal/mol using the following well-known relationships:

$$1 \text{ J/mol} = 0.239006 \text{ cal/mol} \quad \text{and} \quad 1000 \text{ J} = 1 \text{ kJ.}$$

See Gordon, A.J. et al., The Chemist's Companion, John Wiley & Sons, pp. 456-463, (1972), which is incorporated by reference herein in its entirety.

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Solubility parameters have also been tabulated for a wide variety of chemical materials. Tabulations of solubility parameters are found in the above-cited Handbook of Solubility Parameters. Also, see "Solubility Effects In Product, Package, Penetration, And Preservation", C.D. Vaughan, Cosmetics and Toiletries, vol. 103, October 1988, pp. 47-69, which is incorporated by reference herein in its entirety.

Nonlimiting examples of conditioning agents useful as oil soluble conditioning agents include those selected from the group consisting of mineral oil, petrolatum, C7-C40 branched chain hydrocarbons, C1-C30 alcohol esters of C1-C30 carboxylic acids, C1-C30 alcohol esters of C2-C30 dicarboxylic acids, monoglycerides of C1-C30 carboxylic acids, diglycerides of C1-C30 carboxylic acids, triglycerides of C1-C30 carboxylic acids, ethylene glycol monoesters of C1-C30 carboxylic acids, ethylene glycol diesters of C1-C30 carboxylic acids, propylene glycol monoesters of C1-C30 carboxylic acids, propylene glycol diesters of C1-C30 carboxylic acids, C1-C30 carboxylic acid monoesters and polyesters of sugars, polydialkylsiloxanes, polydiarylsiloxanes, polyalkarylsiloxanes, cyclomethicones having 3 to 9 silicon atoms, vegetable oils, hydrogenated vegetable oils, polypropylene glycol C4-C20 alkyl ethers, di C8-C30 alkyl ethers, and mixtures thereof.

Mineral oil, which is also known as petrolatum liquid, is a mixture of liquid hydrocarbons obtained from petroleum. See The Merck Index, Tenth Edition, Entry 7048, p. 1033 (1983) and International Cosmetic Ingredient Dictionary, Fifth Edition, vol. 1, p.415-417 (1993), which are incorporated by reference herein in their entirety.

Petrolatum, which is also known as petroleum jelly, is a colloidal system of nonstraight-chain solid hydrocarbons and high-boiling liquid hydrocarbons, in which most of the liquid hydrocarbons are held inside the micelles. See The Merck Index, Tenth Edition, Entry 7047, p. 1033 (1983); Schindler, Drug Cosmet. Ind., 89, 36-37, 76, 78-80, 82 (1961); and International Cosmetic Ingredient Dictionary, Fifth Edition, vol. 1, p. 537 (1993), which are incorporated by reference herein in their entirety.

Straight and branched chain hydrocarbons having from about 7 to about 40 carbon atoms are useful herein. Nonlimiting examples of these hydrocarbon materials include dodecane, isododecane, squalane, cholesterol, hydrogenated polyisobutylene, docosane (i.e. a C₂₂ hydrocarbon), hexadecane, isohexadecane (a commercially available hydrocarbon sold as Permethyl® 101A by Presperse, South Plainfield, NJ). Also useful are the C7-C40 isoparaffins, which are C7-C40 branched hydrocarbons.

Also useful are C1-C30 alcohol esters of C1-C30 carboxylic acids and of C2-C30 dicarboxylic acids, including straight and branched chain materials as well as

aromatic derivatives. Also useful are esters such as monoglycerides of C1-C30 carboxylic acids, diglycerides of C1-C30 carboxylic acids, triglycerides of C1-C30 carboxylic acids, ethylene glycol monoesters of C1-C30 carboxylic acids, ethylene glycol diesters of C1-C30 carboxylic acids, propylene glycol monoesters of C1-C30 carboxylic acids, and propylene glycol diesters of C1-C30 carboxylic acids. Straight chain, branched chain and aryl carboxylic acids are included herein. Also useful are propoxylated and ethoxylated derivatives of these materials. Nonlimiting examples include diisopropyl sebacate, diisopropyl adipate, isopropyl myristate, isopropyl palmitate, myristyl propionate, ethylene glycol distearate, 2-ethylhexyl palmitate, isodecyl neopentanoate, di-2-ethylhexyl maleate, cetyl palmitate, myristyl myristate, stearyl stearate, cetyl stearate, behenyl behenrate, dioctyl maleate, dioctyl sebacate, diisopropyl adipate, cetyl octanoate, diisopropyl dilinoleate, caprylic/capric triglyceride, PEG-6 caprylic/capric triglyceride, PEG-8 caprylic/capric triglyceride, and mixtures thereof.

Also useful are various C1-C30 monoesters and polyesters of sugars and related materials. These esters are derived from a sugar or polyol moiety and one or more carboxylic acid moieties. Depending on the constituent acid and sugar, these esters can be in either liquid or solid form at room temperature. Examples of liquid esters include: glucose tetraoleate, the glucose tetraesters of soybean oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoleate, sucrose hexaoleate, sucrose hepatoleate, sucrose octaoleate, and mixtures thereof. Examples of solid esters include: sorbitol hexaester in which the carboxylic acid ester moieties are palmitoleate and arachidate in a 1:2 molar ratio; the octaester of raffinose in which the carboxylic acid ester moieties are linoleate and behenate in a 1:3 molar ratio; the heptaester of maltose wherein the esterifying carboxylic acid moieties are sunflower seed oil fatty acids and lignocerate in a 3:4 molar ratio; the octaester of sucrose wherein the esterifying carboxylic acid moieties are oleate and behenate in a 2:6 molar ratio; and the octaester of sucrose wherein the esterifying carboxylic acid moieties are laurate, linoleate and behenate in a 1:3:4 molar ratio. A preferred solid material is sucrose polyester in which the degree of esterification is 7-8, and in which the fatty acid moieties are C18 mono- and/or di-unsaturated and behenic, in a molar ratio of unsaturates:behenic of 1:7 to 3:5. A particularly preferred solid sugar polyester is the octaester of sucrose in which there are about 7 behenic fatty acid moieties and about 1 oleic acid moiety in the molecule.

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Other materials include cottonseed oil or soybean oil fatty acid esters of sucrose. The ester materials are further described in, U.S. Patent No. 2,831,854, U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977; U.S. Patent No. 4,005,195, to Jandacek, issued January 25, 1977, U.S. Patent No. 5,306,516, to Letton et al., issued April 26, 1994; U.S. Patent No. 5,306,515, to Letton et al., issued April 26, 1994; U.S. Patent No. 5,305,514, to Letton et al., issued April 26, 1994; U.S. Patent No. 4,797,300, to Jandacek et al., issued January 10, 1989; U.S. Patent No. 3,963,699, to Rizzi et al, issued June 15, 1976; U.S. Patent No. 4,518,772, to Volpenhein, issued May 21, 1985; and U.S. Patent No. 4,517,360, to Volpenhein, issued May 21, 1985; all of which are incorporated by reference herein in their entirety.

Nonvolatile silicones such as polydialkylsiloxanes, polydiarylsiloxanes, and polyalkarylsiloxanes are also useful oils. These silicones are disclosed in U.S. Patent No. 5,069,897, to Orr, issued December 3, 1991, which is incorporated by reference herein in its entirety. The polyalkylsiloxanes correspond to the general chemical formula $R_3SiO[R_2SiO]_xSiR_3$ wherein R is an alkyl group (preferably R is methyl or ethyl, more preferably methyl) and x is an integer up to about 500, chosen to achieve the desired molecular weight. Commercially available polyalkylsiloxanes include the polydimethylsiloxanes, which are also known as dimethicones, nonlimiting examples of which include the Vicasil[®] series sold by General Electric Company and the Dow Corning[®] 200 series sold by Dow Corning Corporation. Specific examples of polydimethylsiloxanes useful herein include Dow Corning[®] 225 fluid having a viscosity of 10 centistokes and a boiling point greater than 200°C, and Dow Corning[®] 200 fluids having viscosities of 50, 350, and 12,500 centistokes, respectively, and boiling points greater than 200°C. Also useful are materials such as trimethylsiloxysilicate, which is a polymeric material corresponding to the general chemical formula $[(CH_3)_3SiO_{1/2}]_x[SiO_2]_y$, wherein x is an integer from about 1 to about 500 and y is an integer from about 1 to about 500. A commercially available trimethylsiloxysilicate is sold as a mixture with dimethicone as Dow Corning[®] 593 fluid. Also useful herein are dimethiconols, which are hydroxy terminated dimethyl silicones. These materials can be represented by the general chemical formulas $R_3SiO[R_2SiO]_xSiR_2OH$ and $HOR_2SiO[R_2SiO]_xSiR_2OH$ wherein R is an alkyl group (preferably R is methyl or ethyl, more preferably methyl) and x is an integer up to about 500, chosen to achieve the desired molecular weight. Commercially available dimethiconols are typically sold as mixtures with dimethicone or cyclomethicone (e.g. Dow Corning[®] 1401, 1402, and 1403 fluids). Also useful herein are polyalkylaryl siloxanes, with polymethylphenyl siloxanes having viscosities

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from about 15 to about 65 centistokes at 25°C being preferred. These materials are available, for example, as SF 1075 methylphenyl fluid (sold by General Electric Company) and 556 Cosmetic Grade phenyl trimethicone fluid (sold by Dow Corning Corporation).

Vegetable oils and hydrogenated vegetable oils are also useful herein. Examples of vegetable oils and hydrogenated vegetable oils include safflower oil, castor oil, coconut oil, cottonseed oil, menhaden oil, palm kernel oil, palm oil, peanut oil, soybean oil, rapeseed oil, linseed oil, rice bran oil, pine oil, sesame oil, sunflower seed oil, hydrogenated safflower oil, hydrogenated castor oil, hydrogenated coconut oil, hydrogenated cottonseed oil, hydrogenated menhaden oil, hydrogenated palm kernel oil, hydrogenated palm oil, hydrogenated peanut oil, hydrogenated soybean oil, hydrogenated rapeseed oil, hydrogenated linseed oil, hydrogenated rice bran oil, hydrogenated sesame oil, hydrogenated sunflower seed oil, and mixtures thereof.

Also useful are C4-C20 alkyl ethers of polypropylene glycols, C1-C20 carboxylic acid esters of polypropylene glycols, and di-C8-C30 alkyl ethers. Nonlimiting examples of these materials include PPG-14 butyl ether, PPG-15 stearyl ether,, dioctyl ether, dodecyl octyl ether, and mixtures thereof.

WEIGHT RATIOS AND WEIGHT PERCENTAGES

In the present invention, the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than about 20:1, preferably less than about 10:1, preferably less than about 5:1, and more preferably less than about 2:1.

In certain embodiments of the present invention, the cleansing and conditioning component, which is defined as comprising a lathering surfactant and an oil soluble conditioning agent, the lathering surfactant comprises from about 1% to about 75%, preferably from about 10% to about 65%, and more preferably from about 15% to about 45%, by weight of the cleansing and conditioning component, and the oil soluble conditioning agent comprises from about 5% to about 99%, preferably from about 7.5% to about 50%, and more preferably from about 10% to about 30%, by weight of the cleansing and conditioning component.

ADDITIONAL INGREDIENTS

The products of the present invention can comprise a wide range of optional ingredients. Some of these ingredients are listed in more detail herein. Particularly useful are various active ingredients useful for delivering various benefits of the skin or hair during the cleansing and conditioning process. In these compositions, the product is useful for delivering the active ingredient to the skin or hair.

ACTIVE INGREDIENTS

The compositions of the present invention can comprise a safe and effective amount of one or more active ingredients or pharmaceutically-acceptable salts thereof.

The term "safe and effective amount" as used herein, means an amount of an active ingredient high enough to modify the condition to be treated or to deliver the desired skin benefit, but low enough to avoid serious side effects, at a reasonable benefit to risk ratio within the scope of sound medical judgment. What is a safe and effective amount of the active ingredient will vary with the specific active, the ability of the active to penetrate through the skin, the age, health condition, and skin condition of the user, and other like factors.

The active ingredients useful herein can be categorized by their therapeutic benefit or their postulated mode of action. However, it is to be understood that the active ingredients useful herein can in some instances provide more than one therapeutic benefit or operate via more than one mode of action. Therefore, classifications herein are made for the sake of convenience and are not intended to limit the active ingredient to that particular application or applications listed. Also, pharmaceutically-acceptable salts of these active ingredients are useful herein. The following active ingredients are useful in the compositions of the present invention.

Anti-Acne Actives: Examples of useful anti-acne actives include the keratolytics such as salicylic acid (o-hydroxybenzoic acid), derivatives of salicylic acid such as 5-octanoyl salicylic acid, and resorcinol; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); sulfur-containing D and L amino acids and their derivatives and salts, particularly their N-acetyl derivatives, a preferred example of which is N-acetyl-L-cysteine; lipoic acid; antibiotics and antimicrobials such as benzoyl peroxide, octopirox, tetracycline, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorobanilide, azelaic acid and its derivatives, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, ethyl acetate, clindamycin and meclocycline; sebastats such as flavonoids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate.

Anti-Wrinkle and Anti-Skin Atrophy Actives: Examples of antiwrinkle and anti-skin atrophy actives include retinoic acid and its derivatives (e.g., cis and trans); retinol; retinyl esters; niacinamide, salicylic acid and derivatives thereof; sulfur-containing D and L amino acids and their derivatives and salts, particularly the N-acetyl derivatives, a preferred example of which is N-acetyl-L-cysteine; thiols, e.g. ethane thiol; hydroxy acids, phytic acid, lipoic acid; lysophosphatidic acid, and skin peel agents (e.g., phenol and the like).

Non-Steroidal Anti-Inflammatory Actives (NSAIDS): Examples of NSAIDS include the following categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in U.S. Patent 4,985,459 to Sunshine et al., issued January 15, 1991, incorporated by reference herein in its entirety. Examples of useful NSAIDS include acetyl salicylic acid, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen, fenbufen, ketoprofen, indoprofen, piroprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tiroxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like.

Topical Anesthetics: Examples of topical anesthetic drugs include benzocaine, lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexycaine, procaine, cocaine, ketamine, pramoxine, phenol, and pharmaceutically acceptable salts thereof.

Artificial Tanning Agents and Accelerators. Examples of artificial tanning agents and accelerators include dihydroxyacetone, tyrosine, tyrosine esters such as ethyl tyrosinate, and phospho-DOPA.

Antimicrobial and Antifungal Actives: Examples of antimicrobial and antifungal actives include β -lactam drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorobanilide, phenoxyethanol, phenoxy propanol, phenoxyisopropanol, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, hexamidine isethionate, metronidazole, pentamidine, gentamicin, kanamycin, lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin, paromomycin, streptomycin, tobramycin, miconazole, tetracycline hydrochloride, erythromycin, zinc erythromycin, erythromycin estolate, erythromycin stearate, amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride, neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amanfadine hydrochloride, amanfadine sulfate, octopirox, parachlorometa xyleneol, nystatin, tolnaftate, zinc pyrithione and clotrimazole.

Preferred examples of actives useful herein include those selected from the group consisting of salicylic acid, benzoyl peroxide, 3-hydroxy benzoic acid, glycolic acid, lactic acid, 4-hydroxy benzoic acid, acetyl salicylic acid, 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, 2-hydroxyhexanoic acid, cis-retinoic acid, trans-retinoic acid, retinol, phytic acid, N-acetyl-L-cysteine, lipoic acid, azelaic acid, arachidonic acid, benzoylperoxide, tetracycline, ibuprofen, naproxen, hydrocortisone, acetaminophen, resorcinol, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorocarbanilide, octopirox, lidocaine hydrochloride, clotrimazole, miconazole, neocycin sulfate, and mixtures thereof.

Sunscreen Actives: Also useful herein are sunscreensing actives. A wide variety of sunscreensing agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety. Nonlimiting examples of sunscreens which are useful in the compositions of the present invention are those selected from the group consisting of 2-ethylhexyl *p*-methoxycinnamate, 2-ethylhexyl *N,N*-dimethyl-*p*-aminobenzoate, *p*-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-*t*-butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof. Still other useful sunscreens are those disclosed in U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991; these two references are incorporated by reference herein in their entirety. Especially preferred examples of these sunscreens include those selected from the group consisting of 4-*N,N*-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone, 4-*N,N*-(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-*N,N*-(2-ethylhexyl)-methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-*N,N*-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof. Exact amounts of sunscreens which can be employed will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF) to be achieved. SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

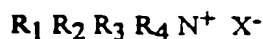
Nonlimiting examples of preferred actives useful herein include those selected from the group consisting of salicylic acid, benzoyl peroxide, niacinamide, cis-retinoic acid, trans-retinoic acid, retinol, retinyl palmitate, phytic acid, N-acetyl L-cysteine, azelaic acid, lipoic acid, resorcinol, lactic acid, glycolic acid, ibuprofen, naproxen, hydrocortisone, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorocarbanilide, 2-ethylhexyl *p*-methoxycinnamic acid, oxybenzone, 2-phenylbenzimidazole-5-sulfonic acid, dihydroxyacetone, and mixtures thereof.

Cationic Surfactants

The products of the present invention can also optionally comprise one or more cationic surfactants, provided these materials are selected so as not to interfere with the overall lathering characteristics of the required, lathering surfactants.

Nonlimiting examples of cationic surfactants useful herein are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; and McCutcheon's, Functional Materials, North American Edition (1992); both of which are incorporated by reference herein in their entirety.

Nonlimiting examples of cationic surfactants useful herein include cationic alkyl ammonium salts such as those having the formula:



wherein R_1 is selected from an alkyl group having from about 12 to about 18 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 18 carbon atoms; R_2 , R_3 , and R_4 are independently selected from hydrogen, an alkyl group having from about 1 to about 18 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 18 carbon atoms; and X is an anion selected from chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, methyl sulfate, ethyl sulfate, tosylate, lactate, citrate, glycolate, and mixtures thereof. Additionally, the alkyl groups can also contain ether linkages, or hydroxy or amino group substituents (e.g., the alkyl groups can contain polyethylene glycol and polypropylene glycol moieties).

More preferably, R_1 is an alkyl group having from about 12 to about 18 carbon atoms; R_2 is selected from H or an alkyl group having from about 1 to about 18 carbon atoms; R_3 and R_4 are independently selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described in the previous paragraph.

Most preferably, R_1 is an alkyl group having from about 12 to about 18 carbon atoms; R_2 , R_3 , and R_4 are selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described previously.

Alternatively, other useful cationic surfactants include amino-amides, wherein in the above structure R_1 is alternatively $R_5CO-(CH_2)_n-$, wherein R_5 is an alkyl group having from about 12 to about 22 carbon atoms, and n is an integer from about 2 to about 6, more preferably from about 2 to about 4, and most preferably from about 2 to about 3. Nonlimiting examples of these cationic emulsifiers include stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Nonlimiting examples of quaternary ammonium salt cationic surfactants include those selected from the group consisting of cetyl ammonium chloride, cetyl ammonium bromide, lauryl ammonium chloride, lauryl ammonium bromide, stearyl ammonium chloride, stearyl ammonium bromide, cetyl dimethyl ammonium chloride, cetyl dimethyl ammonium bromide, lauryl dimethyl ammonium chloride, lauryl dimethyl ammonium bromide, stearyl dimethyl ammonium chloride, stearyl dimethyl ammonium bromide, cetyl trimethyl ammonium chloride, cetyl trimethyl ammonium bromide, lauryl trimethyl ammonium chloride, lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium chloride, stearyl trimethyl ammonium bromide, lauryl dimethyl ammonium chloride, stearyl dimethyl cetyl ditallow dimethyl ammonium chloride, dicetyl ammonium chloride, dicetyl ammonium bromide, dilauryl ammonium chloride, dilauryl ammonium bromide, distearyl ammonium chloride, distearyl ammonium bromide, dicetyl methyl ammonium chloride, dicetyl methyl ammonium bromide, dilauryl methyl ammonium chloride, dilauryl methyl ammonium bromide, distearyl methyl ammonium chloride, distearyl dimethyl ammonium chloride, distearyl methyl ammonium bromide, and mixtures thereof. Additional quaternary ammonium salts include those wherein the C12 to C22 alkyl carbon chain is derived from a tallow fatty acid or from a coconut fatty acid. The term "tallow" refers to an alkyl group derived from tallow fatty acids (usually hydrogenated tallow fatty acids), which generally have mixtures of alkyl chains in the C16 to C18 range. The term "coconut" refers to an alkyl group derived from a coconut fatty acid, which generally have mixtures of alkyl chains in the C12 to C14 range. Examples of quaternary ammonium salts derived from these tallow and coconut sources include ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate,

di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl)dimethyl ammonium chloride, di(coconutalkyl)dimethyl ammonium bromide, tallow ammonium chloride, coconut ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Preferred cationic surfactants useful herein include those selected from the group consisting of dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, and mixtures thereof.

Water Soluble Conditioning Agents

The present invention can also optionally comprise water soluble conditioning agents. Nonlimiting examples of conditioning agents useful as water soluble conditioning agents include those selected from the group consisting of polyhydric alcohols, polypropylene glycols, polyethylene glycols, ureas, pyrrolidone carboxylic acids, ethoxylated and/or propoxylated C3-C6 diols and triols, alpha-hydroxy C2-C6 carboxylic acids, ethoxylated and/or propoxylated sugars, polyacrylic acid copolymers, sugars having up to about 12 carbon atoms, sugar alcohols having up to about 12 carbon atoms, and mixtures thereof. Specific examples of useful water soluble conditioning agents include materials such as urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); sucrose, fructose, glucose, erythrose, erythritol, sorbitol, mannitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol, and the like; polyethylene glycols such as PEG-2, PEG-3, PEG-30, PEG-50, polypropylene glycols such as PPG-9, PPG-12, PPG-15, PPG-17, PPG-20, PPG-26, PPG-30, PPG-34; alkoxylated glucose; hyaluronic acid; and mixtures thereof. Also useful are materials such as aloe vera in any of its variety of forms (e.g., aloe vera gel), chitin, starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500, and IM-2500 (available from Celanese Superabsorbent Materials, Portsmouth, VA); lactamide monoethanolamine; acetamide monoethanolamine; and mixtures thereof. Also useful are propoxylated glycerols as described in propoxylated glycerols described in U.S. Patent No. 4,976,953, to Orr et al., issued December 11, 1990, which is incorporated by reference herein in its entirety.

Other Optional Ingredients

The compositions of the present invention can comprise a wide range of other optional components. These additional components should be pharmaceutically acceptable. The CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, which is incorporated by reference herein in its entirety, describes a wide variety of nonlimiting cosmetic and pharmaceutical ingredients commonly used in the skin care industry, which are suitable for use in the compositions of the present invention. Nonlimiting examples of functional classes of ingredients are described at page 537 of this reference. Examples of these and other functional classes include: abrasives, absorbents, anticaking agents, antioxidants, vitamins, binders, biological additives, buffering agents, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers, fragrance components, humectants, opacifying agents, pH adjusters, preservatives, propellants, reducing agents, skin bleaching agents, and sunscreens agents.

Also useful herein are aesthetic components such as fragrances, pigments, colorings, essential oils, skin sensates, astringents, skin soothing agents, and skin healing agents.

METHODS OF MANUFACTURE

The disposable, single use personal care cleansing and conditioning products of the present invention are manufactured by separately or simultaneously adding onto or impregnating into a water insoluble substrate a lathering surfactant and a conditioning agent, wherein said resulting product is substantially dry. By "separately" is meant that the surfactants and conditioning agents can be added sequentially, in any order without first being combined together. By "simultaneously" is meant that the surfactants and conditioning agents can be added at the same time, with or without first being combined together.

For example, the lathering surfactants can first be added onto or impregnated into the water insoluble substrate followed by the conditioning agents, or vice versa. Alternatively, the lathering surfactants and conditioning agents can be added onto or impregnated into the water insoluble substrate at the same time. Alternatively, the lathering surfactants and the conditioning agents can be combined together before adding onto or impregnating into the water insoluble substrate.

The surfactant, conditioning agents, and any optional ingredients can be added onto or impregnated into the water insoluble substrate by any means known to those skilled in the art: for example, by spraying, laser printing, splashing, dipping, soaking, or coating.

When water or moisture is used or present in the manufacturing process, the resulting treated substrate is then dried so that it is substantially free of water. The treated substrate can be dried by any means known to those skilled in the art. Nonlimiting examples of known drying means include the use of convection ovens, radiant heat sources, microwave ovens, forced air ovens, and heated rollers or cans. Drying also includes air drying without the addition of heat energy, other than that present in the ambient environment. Also, a combination of various drying methods can be used.

METHODS OF CLEANSING AND CONDITIONING THE SKIN OR HAIR

The present invention also relates to a method of cleansing and conditioning the skin or hair with a personal cleansing product of the present invention. These methods comprise the steps of wetting with water a substantially dry, disposable, single use personal cleansing product comprising a water insoluble substrate, a lathering surfactant, and a conditioning component, and contacting the skin or hair with said wetted product. In further embodiments, the present invention is also useful for delivering various active ingredients to the skin or hair.

The products of the present invention are substantially dry and are intended to be wetted with water prior to use. The product is wetted by immersion in water or by placing it under a stream of water. Lather is generated from the product by mechanically agitating and/or deforming the product either prior to or during contact of the product with the skin or hair. The resulting lather is useful for cleansing and conditioning the skin or hair. During the cleansing process and subsequent rinsing with water, the conditioning agents and active ingredients are deposited onto the skin or hair. Deposition of conditioning agents and active ingredients are enhanced by the physical contact of the substrate with the skin or hair.

DEPOSITION OF THE CONDITIONING COMPONENT AND ANY ACTIVE INGREDIENTS ONTO THE SKIN OR HAIR

The compositions of the present invention are useful for depositing the conditioning components of the present invention to the skin or hair. In further embodiments where an active ingredient is present, the compositions are also useful for depositing the active ingredient to the skin or hair.

The compositions of the present invention preferably deposit greater than about 2.5 micrograms/cm², more preferably greater than about 5 micrograms/cm², more preferably greater than about 10 micrograms/cm², and most preferably greater than about 25 micrograms/cm² of the conditioning component to the skin or hair during use of the product.

ingredients and then cooled to 45°C. The Phase C ingredients are then mixed together in a separate vessel at room temperature. Next, the Phase C mixture is added into the vessel containing the combination of Phases A and B at room temperature. 1.5 grams of the resulting solution is sprayed onto each substrate. Alternatively, the substrate can be dipped into the resulting solution. The treated substrate is then dried in an oven to constant weight. Alternatively, the treated substrate is dried in a convection oven at 45°C to constant weight.

The resulting cleansing composition is used by wetting with water and is useful for cleansing the skin or hair and for depositing the conditioning agents onto the skin or hair.

In alternative manufacturing procedures, the lathering surfactants, conditioning agents, and optional ingredients can be separately or simultaneously added onto or impregnated into the water insoluble substrate by spraying, laser printing, splashing, dipping, or coating.

In alternative embodiments, other substrates such as woven substrates, hydroentangled substrates, natural sponges, synthetic sponges, or polymeric netted meshes.

Examples 5-8

A personal care cleansing and conditioning product is prepared as follows:

<u>Ingredients</u>	<u>Weight Percent</u>			
	Example 5	Example 6	Example 7	Example 8
<u>Phase A</u>				
Water	QS 100	QS 100	QS 100	QS 100
Glycerin	10.00	10.00	10.00	10.00
Panthenol	0.50	---	0.50	0.50
Sodium Lauroamphoacetate	2.40	2.40	2.40	2.40
Ammonium Lauryl Sulfate	1.40	1.40	1.40	1.40
Polyquarternium-10	0.25	0.25	0.25	0.25
Disodium EDTA	0.10	0.10	0.10	0.10
<u>Phase B</u>				
Sucrose Ester Fatty Acid Cottonate	3.00	3.00	3.00	3.00
Petrolatum	---	---	---	0.50
Cetyl Dimethicone	---	---	---	0.50
Cetyl Ricinoleate	---	2.00	2.00	1.00

SUBSTITUTE SHEET (rule 26)

Phase C

Butylene Glycol	2.00	2.00	2.00	2.00
DMDM Hydantoin (and) Iodopropynyl Carbamate	0.20	0.20	0.20	0.20

Water Insoluble Substrate

A hydroapertured, nonwoven substrate having a basis weight of about 60 gsy comprising 50% rayon and 50% polyester approximately 6 in. by 7.6 in. and a thickness of about 20 mil.

In a suitable vessel, the Phase A ingredients are mixed at room temperature to form a dispersion and heated with stirring to 65°C. The Phase B ingredients are mixed in a separate suitable vessel and heated to 65°C. Once the temperatures are the same, the Phase B ingredients are mixed into the vessel containing the Phase A ingredients and then cooled to 45°C. Next, the Phase C mixture is added into the vessel containing the combination of Phases A and B at room temperature. 1.5 grams of the resulting solution is sprayed onto each substrate. Alternatively, the substrate can be dipped into the resulting solution. The treated substrate is then dried in an oven to constant weight. Alternatively, the treated substrate is dried in a convection oven at 45°C to constant weight.

The resulting cleansing composition is used by wetting with water and is useful for cleansing the skin or hair and for depositing the conditioning agents onto the skin or hair.

In alternative manufacturing procedures, the lathering surfactants, conditioning agents, and optional ingredients can be separately or simultaneously added onto or impregnated into the water insoluble substrate by spraying, laser printing, splashing, dipping, or coating.

In alternative embodiments, other substrates such as woven substrates, hydroentangled substrates, natural sponges, synthetic sponges, or polymeric netted meshes.

The present invention also relate to a method of depositing greater than about 2.5 micrograms/cm², preferably greater than about 5 micrograms/cm², more preferably greater than about 10 micrograms/cm², and most preferably greater than about 25 micrograms/cm² of the conditioning agent to the surface of the skin or hair.

Quantitation of the conditioning component deposited on the skin or hair can be measured using a variety of standard analytical techniques well known to the chemist of ordinary skill in the art. Such methods include for instance extraction of an area of the skin or hair with a suitable solvent followed by analysis by chromatography (i.e. gas chromatography, liquid chromatography, supercritical fluid chromatography, etc.), IR spectroscopy, UV/VIS spectroscopy, mass spectrometry, etc. Direct measurements can also be made on the skin or hair by techniques such as IR spectroscopy, UV/VIS spectroscopy, opacity measurements, fluorescence spectroscopy, ESCA spectroscopy, and the like.

In a typical method for measuring deposition, a product of the present invention is wetted with water and squeezed and agitated to generate a lather. The product is then rubbed for approximately 15 seconds on a site, approximately about 25 cm² to about 300 cm², preferably about 50 cm² to about 100 cm², on the skin or head which has been demarcated using an appropriate indelible marker. The site is then rinsed for approximately 10 seconds and then allowed to air dry for approximately 10 minutes. The site is then either extracted and the extracts analyzed, or analyzed directly using any techniques such as those exemplified above.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. In the following examples, all ingredients are listed at an active level. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Ingredients are identified by chemical or CTFA name.

Examples 1-4

A personal care cleansing and conditioning product is prepared as follows:

<u>Ingredients</u>	<u>Weight Percent</u>			
	Example 1	Example 2	Example 3	Example 4
<u>Phase A</u>				
Water	QS 100	QS 100	QS 100	QS 100
Glycerin	10.00	10.00	10.00	10.00
Disodium Lauroamphodiacetate				
and Sodium Trideceth Sulfate	4.00	4.00	----	----
Sodium Lauroamphoacetate	----	----	2.40	2.40
Sodium Lauroyl Sarcosinate	4.00	4.00	----	----
Ammonium Laureth Sulfate	----	----	4.20	4.20
Ammonium Lauryl Sulfate	----	----	1.40	1.40
Polyquaternium-10	0.25	0.25	0.25	0.25
Disodium EDTA	0.10	0.10	0.10	0.10
<u>Phase B</u>				
Sucrose Ester Fatty Acid Cottonate	3.00	3.00	3.00	3.00
Petrolatum	----	1.50	----	----
Cetyl Dimethicone	----	----	----	2.00
<u>Phase C</u>				
Butylene Glycol	2.00	2.00	2.00	2.00
DMDM Hydantoin (and)	0.20	0.20	0.20	0.20
Iodopropynyl Carbamate				

Water Insoluble Substrate

A hydroapertured, nonwoven substrate having a basis weight of about 60 gsy comprising 50% rayon and 50% polyester approximately 6 in. by 7.6 in. and a thickness of about 20 mil.

In a suitable vessel, the Phase A ingredients are mixed at room temperature to form a dispersion and heated with stirring to 65°C. The Phase B ingredients are mixed in a separate suitable vessel and heated to 65°C. Once the temperatures are the same, the Phase B ingredients are mixed into the vessel containing the Phase A

Examples 9-12

<u>Ingredients</u>	<u>Weight Percent</u>			
	Example 9	Example 10	Example 11	Example 12
<u>Phase A</u>				
Water	QS 100	QS 100	QS 100	QS 100
Disodium Lauroamphodiacetate				
and Sodium Trideceth Sulfate	4.00	4.00	---	---
Sodium Lauroamphoacetate	---	---	2.40	2.40
Sodium Lauroyl Sarcosinate	4.00	4.00	---	---
Ammonium Laureth Sulfate	---	---	4.20	4.20
Ammonium Lauryl Sulfate	---	---	1.40	1.40
Disodium EDTA	0.10	0.10	0.10	0.10
<u>Phase B</u>				
Sucrose Ester Fatty Acid Cottonate	3.00	3.00	3.00	3.00
Petrolatum	---	1.50	---	---
Cetyl Dimethicone	---	---	---	2.00
<u>Phase C</u>				
DMDM Hydantoin (and)	0.20	0.20	0.20	0.20
Iodopropynyl Carbamate				

Water Insoluble Substrate

A hydroapertured, nonwoven substrate having a basis weight of about 60 gsy comprising 50% rayon and 50% polyester approximately 6 in. by 7.6 in. and a thickness of about 20 mil.

In a suitable vessel, the Phase A ingredients are mixed at room temperature to form a dispersion and heated with stirring to 65°C. The Phase B ingredients are mixed in a separate suitable vessel and heated to 65°C. Once the temperatures are the same, the Phase B ingredients are mixed into the vessel containing the Phase A ingredients and then cooled to 45°C. The Phase C ingredients are then mixed together in a separate vessel at room temperature. Next, the Phase C mixture is added into the vessel containing the combination of Phases A and B at room temperature. 1.5 grams of the resulting solution is sprayed each substrate.

SUBSTITUTE SHEET (rule 26)

Alternatively, the substrate can be dipped into the solution. The treated substrate is then dried in an oven to constant weight. Alternatively, the treated substrate is dried in a convection oven at about 45°C to constant weight.

The resulting cleansing composition is used by wetting with water and is useful for cleansing the skin or hair and for depositing the conditioning agents onto the skin or hair.

In alternative manufacturing procedures, the lathering surfactants, conditioning agents, and optional ingredients can be separately or simultaneously added onto or impregnated into the water insoluble substrate by spraying, laser printing, splashing, dipping, or coating.

In alternative embodiments, other substrates such as woven substrates, hydroentangled substrates, natural sponges, synthetic sponges, or polymeric netted meshes.

Examples 13-16

<u>Ingredients</u>	<u>Weight Percent</u>			
	Example 13	Example 14	Example 15	Example 16
<u>Phase A</u>				
Water	QS 100	QS 100	QS 100	QS 100
Sodium Lauroamphoacetate	2.40	2.40	2.40	2.40
Ammonium Laureth Sulfate	4.20	4.20	4.20	4.20
Ammonium Lauryl Sulfate	1.40	1.40	1.40	1.40
Disodium EDTA	0.10	0.10	0.10	0.10
<u>Phase B</u>				
Sucrose Ester Fatty Acid Cottonate	3.00	3.00	3.00	3.00
Petrolatum	----	0.50	1.00	----
Cetyl Dimethicone	----	0.50	----	1.00
Cetyl Ricinoleate	2.00	0.50	1.00	1.00
<u>Phase C</u>				
DMDM Hydantoin (and) Iodopropynyl Carbamate	0.20	0.20	0.20	0.20

Water Insoluble Substrate

A hydroapertured, nonwoven substrate having a basis weight of about 60 gsy comprising 50% rayon and 50% polyester approximately 6 in. by 7.6 in. and a thickness of about 20 mil.

In a suitable vessel, the Phase A ingredients are mixed at room temperature to form a dispersion and heated with stirring to 65°C. The Phase B ingredients are mixed in a separate suitable vessel and heated to 65°C. Once the temperatures are the same, the Phase B ingredients are mixed into the vessel containing the Phase A ingredients and then cooled to 45°C. Next, the Phase C mixture is added into the vessel containing the combination of Phases A and B at room temperature. 1.5 grams of the resulting solution is sprayed onto each substrate. Alternatively, the substrate can be dipped into the solution. The treated substrate is then dried in an oven to constant weight. Alternatively, the treated substrate is dried in a convection oven at about 45°C to constant weight.

The resulting cleansing composition is used by wetting with water and is useful for cleansing the skin or hair and for depositing the conditioning agents onto the skin or hair.

In alternative manufacturing procedures, the lathering surfactants, conditioning agents, and optional ingredients can be separately or simultaneously added onto or impregnated into the water insoluble substrate by spraying, laser printing, splashing, dipping, or coating.

In alternative embodiments, other substrates such as woven substrates, hydroentangled substrates, natural sponges, synthetic sponges, or polymeric netted meshes.

What is claimed is:

1. A disposable, single use personal care cleansing and conditioning product comprising:

- (A) a water insoluble substrate,
- (B) a lathering surfactant, and
- (C) an oil soluble conditioning agent,

wherein said cleansing product deposits greater than $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and wherein said product is substantially dry.

2. A product according to Claim 1 wherein said lathering surfactant comprises from 0.5% to 12.5% by weight of said water insoluble substrate and said oil soluble conditioning agent comprises from 1% to 99% by weight of said water insoluble substrate; preferably wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than 20:1.

3. A product according to Claim 1 or Claim 2 wherein said water insoluble substrate comprises one or more materials selected from the group consisting of silks; keratins; celluloses, preferably wood pulp, cotton, hemp, jute, and flax; acetates, preferably polyvinyl acetates; acrylics, preferably modacrylics; cellulose esters; polyamides, preferably nylons; polyesters; polyolefins, preferably polypropylenes and polyethylenes; polyvinyl alcohols; polyurethanes; rayon; and mixtures thereof.

4. A product according to any of Claims 1 to 3 wherein said water insoluble substrate is selected from the group consisting of nonwoven substrates, preferably, a nonwoven sheet of fibers selected from the group consisting of rayon fibers, cellulose fibers, polyester fibers, and mixtures thereof; woven substrates; hydroentangled substrates; natural sponges; synthetic sponges; polymeric netted meshes; formed films; and mixtures thereof.

5. A product according to any of Claims 1 to 4 wherein said water insoluble substrate comprises two or more sheets of fibers each in turn having different textures.

6. A product according to any of Claims 1 to 5 wherein said lathering surfactant is selected from the group consisting of anionic lathering surfactants, preferably said anionic lathering surfactant is selected from the group consisting of sarcosinates, sulfates, isethionates, phosphates, taurates, and mixtures thereof, more preferably said anionic lathering surfactant is selected from the group consisting of ammonium lauroyl sarcosinate, sodium trideceth sulfate, sodium lauroyl sarcosinate, ammonium laureth sulfate, sodium laureth sulfate, ammonium lauryl sulfate, sodium lauryl sulfate, ammonium cocoyl isethionate, sodium cocoyl isethionate, sodium lauroyl isethionate, sodium cetyl sulfate, and mixtures thereof; nonionic lathering surfactants, preferably said nonionic lathering surfactant is selected from the group consisting of amine oxides, alkyl glucosides, alkyl polyglucosides, polyhydroxy fatty acid amides, alkoxylated fatty acid esters, sucrose esters, and mixtures thereof, more preferably said nonionic lathering surfactant is selected from the group consisting of lauramine oxide, cocoamine oxide, decyl polyglucose, lauryl polyglucose, C12-14 glucose amides, sucrose cocoate, sucrose laurate, and mixtures thereof; amphoteric lathering surfactants, preferably said amphoteric lathering surfactant is selected from the group consisting of betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanoates, aminoalkanoates, and mixtures thereof, more preferably said amphoteric lathering surfactant is selected from the group consisting of disodium lauroamphodiacetate, sodium lauroamphoacetate, cetyl dimethyl betaine, cocoamidopropyl betaine, cocoamidopropyl hydroxy sultaine, and mixtures thereof; and mixtures thereof.

7. A product according to any of Claims 1 to 6 wherein said oil soluble conditioning agent is selected from one or more oil soluble conditioning agents such that the weighted arithmetic mean solubility parameter of said oil soluble conditioning agent is less than or equal to 10.5, preferably said oil soluble conditioning agent is selected from the group consisting of esters of fatty acids, polyol polyesters, glycerin mono-esters, glycerin di-esters, glycerin tri-esters, epidermal and sebaceous hydrocarbons, lanolin, mineral oil, silicone oil, silicone gum, vegetable oil, vegetable oil adduct, petrolatum, nonionic polymers, and mixtures thereof.

8. A product according to any of Claims 1 to 7 wherein said cleansing product further comprises a safe and effective amount of one or more active ingredients selected from the group consisting of anti-acne actives, preferably salicylic acid, resorcinol, cis-retinoic acid, trans-retinoic acid, N-acetyl L-cysteine, lipoic acid, benzoyl peroxide, azelaic acid, phenoxyethanol, phenoxypropanol, and phenoxyisopropanol; anti-wrinkle and anti-skin actives, preferably cis-retinoic acid, trans-retinoic acid, retinol, retinyl palmitate, niacinamide, salicylic acid, N-acetyl L-cysteine, phytic acid, lipoic acid, glycolic acid, and lactic acid; non-stearoidal anti-inflammatory actives, preferably ibuprofen, naproxen, and hydrocortisone; topical anesthetics; artificial tanning agents and accelerators, preferably dihydroxyacetone; anti-microbial and anti-fungal agents, preferably 2,4,4'-trichloro-2'-hydroxy diphenyl ether and 3,4,4'-trichlorocarbaniide; sunscreen actives, preferably 2-ethylhexyl *p*-methoxycinnamic acid, oxybenzone, and 2-phenylbenzimidazole-5-sulfonic acid; anti-oxidants and mixtures thereof.

9. A disposable, single use personal care cleansing and conditioning product comprising:

(A) a water insoluble substrate, and

(B) a cleansing and conditioning composition comprising:

(i) a lathering surfactant, preferably comprising from 1% to 75% by weight of said cleansing and conditioning composition, and

(ii) an oil soluble conditioning agent, preferably comprising from 5% to 99% by weight of said cleansing and conditioning composition,

wherein said lathering surfactant and said oil soluble conditioning agent are separately or simultaneously added onto or impregnated into said water insoluble substrate, and wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than 20:1,

wherein said cleansing product deposits greater than $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and

wherein said product is substantially dry.

10. A method of manufacturing a disposable, single use personal care cleansing and conditioning product comprising the step of separately or simultaneously adding onto or impregnating into a water insoluble substrate, preferably by spraying, laser printing, splashing, dipping, or coating,

(A) a lathering surfactant, and

(B) an oil soluble conditioning agent,

wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than 20:1,

wherein said cleansing product deposits greater than $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent to the surface of the skin or hair, and

wherein said resulting product is substantially dry.

11. A method of manufacturing a product according to Claim 10 wherein said lathering surfactant and said oil soluble conditioning agent are combined together before being added onto or impregnated into said water insoluble substrate.

12. A method of depositing greater than $2.5 \mu\text{g}/\text{cm}^2$ of an oil soluble conditioning agent to the surface of the skin or hair by contacting the product of any of Claims 1 to 9 with said skin or hair.

13. A method of cleansing and conditioning the skin or hair with a personal cleansing product, comprising the steps of:

(A) wetting with water a substantially dry, disposable, single use personal cleansing product comprising:

(i) a water insoluble substrate,

(ii) a lathering surfactant, and

(iii) an oil soluble conditioning agent,

wherein the weight ratio of the lathering surfactant to the oil soluble conditioning agent is less than 20:1, and

(B) contacting the skin or hair with said wetted product

wherein said cleansing product deposits greater than $2.5 \mu\text{g}/\text{cm}^2$ of said oil soluble conditioning agent onto the surface of the skin or hair.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/19256

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 00116 A (PROCTER & GAMBLE) 5 January 1995 see the whole document ---	1-4,6-13
P, A	WO 97 07781 A (UNILEVER PLC ; UNILEVER NV (NL)) 6 March 1997 see examples 1,2 ---	1-4,6-13
A	WO 96 24723 A (KIMBERLY CLARK CO) 15 August 1996 see the whole document ---	1-4,6-13
A	GB 2 218 430 A (TOP LINE DEVELOPMENTS LIMITED) 15 November 1989 see the whole document ---	1-4,6-13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 97/19256

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 613 675 A (JOHNSON & JOHNSON CONSUMER) 7 September 1994 see the whole document ----	1-4,6-13
A	WO 96 24329 A (PROCTER & GAMBLE) 15 August 1996 see the whole document ----	1-4,6-13
A	WO 95 16824 A (PROCTER & GAMBLE) 22 June 1995 see examples ----	1-4,6-13
A	WO 96 14835 A (PROCTER & GAMBLE) 23 May 1996 see the whole document -----	1-4,6-13

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INTERNATIONAL SEARCH REPORT

information on patent family members

Int. Application No

PCT/US 97/19256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9500116 A	05-01-95	BR 9406807 A CA 2165050 A CN 1135174 A EP 0702550 A JP 8511962 T US 5650384 A	23-07-96 05-01-95 06-11-96 27-03-96 17-12-96 22-07-97
WO 9707781 A	06-03-97	AU 6927496 A	19-03-97
WO 9624723 A	15-08-96	US 5665426 A AU 4968696 A CA 2210338 A EP 0808389 A US 5650218 A	09-09-97 27-08-96 15-08-96 26-11-97 22-07-97
GB 2218430 A	15-11-89	NONE	
EP 0613675 A	07-09-94	AU 682333 B AU 5756194 A BR 9400829 A CA 2117136 A ZA 9401547 A	02-10-97 08-09-94 01-11-94 06-09-94 04-09-95
WO 9624329 A	15-08-96	US 5648083 A AU 4767296 A EP 0808151 A ZA 9601067 A	15-07-97 27-08-96 26-11-97 16-07-96
WO 9516824 A	22-06-95	AU 1295895 A EP 0734474 A JP 9506682 T US 5525345 A	03-07-95 02-10-96 30-06-97 11-06-96
WO 9614835 A	23-05-96	AU 4018095 A EP 0792144 A FI 971966 A NO 972106 A ZA 9509483 A	06-06-96 03-09-97 07-05-97 20-06-97 28-05-96